

Large magnetic heat transport in a Haldane chain material $\text{Ni}(\text{C}_3\text{H}_{10}\text{N}_2)_2\text{NO}_2\text{ClO}_4$

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We report a study on the heat transport of an $S = 1$ Haldane chain compound $\text{Ni}(\text{C}_3\text{H}_{10}\text{N}_2)_2\text{NO}_2\text{ClO}_4$ at low temperatures and in magnetic fields. The zero-field thermal conductivities show a remarkable anisotropy for the heat current along the spin-chain direction (κ_b) and the vertical direction (κ_c), implying a magnetic contribution to the heat transport along the spin-chain direction. The magnetic-field-induced change of the spin spectrum has obviously opposite impacts on κ_b and κ_c . In particular, $\kappa_b(H)$ and $\kappa_c(H)$ curves show peak-like increases and dip-like decreases, respectively, at ~ 9 T, which is the critical field that minimizes the spin gap. These results indicate a large magnetic thermal transport in this material.

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The heat transport in one-dimensional (1D) quantum magnets has attracted much attention due to the role of magnetic excitations.^{1–3} Theoretical and experimental results have made an agreement that the $S = 1/2$ Heisenberg chain system, which is an integrable spin model, exhibits a ballistic transport of the spin excitations.^{4–9} However, the situation of the $S = 1$ chain system is not clear yet. Several theories on this nonintegrable spin model predicted either a diffusive or a ballistic transport of spin excitations.^{4,10–12} The experimental results on the $S = 1$ Haldane chain materials AgVP_2S_6 and Y_2BaNiO_5 showed considerably small magnetic thermal conductivity and therefore seemed to support the model of diffusive spin transport.^{13,14} However, a large magnetic thermal conductivity has been revealed in a two-leg Heisenberg $S = 1/2$ ladder compound $(\text{La}, \text{Sr}, \text{Ca})_{14}\text{Cu}_{24}\text{O}_{41}$,^{15,16} which potentially shows the evidence of a ballistic behavior. This is surprising because the $S = 1$ chain and the $S = 1/2$ ladder are essentially the same in the aspects of the spin-liquid ground state and the gapped magnetic spectrum.¹⁷ In a recent work on an organic $S = 1$ Haldane chain compound $\text{Ni}(\text{C}_2\text{H}_8\text{N}_2)_2\text{NO}_2\text{ClO}_4$ (abbreviated as NENP), which has relatively weaker spin interaction and smaller spin gap (~ 12.2 K),^{18,19} the magnetic heat transport was found to be rather large.²⁰ Since the spin transport of NENP can only be observed in magnetic field, which weakens the spin gap,²⁰ it is possible that the large spin transport in zero magnetic field can be found in $S = 1$ chain systems with smaller energy gaps.

$\text{Ni}(\text{C}_3\text{H}_{10}\text{N}_2)_2\text{NO}_2\text{ClO}_4$ (abbreviated as NINO), which was found to be another ideal $S = 1$ Haldane chain system, has a similar spin structure to that of NENP (see Fig. 1). The Ni^{2+} spins ($S = 1$) form the spin chains along the b axis, in which the intrachain antiferromag-

netic (AF) interaction ($J \approx 50$ K) is about a factor of 10^4 times stronger than the interchain interaction (J').^{21–24} It is known that in an isotropic AF $S = 1$ chain system, the spin excitations are triply degenerate with an energy gap $E_g \approx 0.41J$, which is about 20.3 K for NINO.²⁵ However, due to the strong planar anisotropy and weak orthorhombic anisotropy, the Haldane gap is split into three gaps with zero-field values $\Delta E_1 = 8.3$ K, $\Delta E_2 = 12.5$ K and $\Delta E_3 = 21.9$ K.²² When an external magnetic field is applied along the a axis, ΔE_2 keeps constant, ΔE_3 increases, and ΔE_1 decreases. The smallest gap ΔE_1 is apparently the most important for the low-energy magnetic excitations. In particular, ΔE_1 descends to a small value at a critical field $H_c \approx 9$ T, and then increases above H_c .^{23,24} In general, magnetic properties of NINO are very similar to those of NENP, except that the energy scales of the spin gap are different.

In this work, we study the heat transport of NINO single crystals at low temperatures down to 0.3 K and in magnetic fields up to 14 T. It is found that thermal conductivities show a remarkable anisotropy between the direction along the spin chain and that perpendicular to it, which indicates a large magnetic contribution to the heat transport along the spin-chain direction.

High-quality NINO single crystals were grown by a slow evaporation method from aqueous solution.²⁶ The largest surfaces of the as-grown crystals are parallel to the bc plane, confirmed by the X-ray diffraction. Therefore, it is possible to obtain large parallelepiped-shaped samples with the longest dimension along the b axis or the c axis. The thermal conductivities were measured using a conventional steady-state technique along the b axis (κ_b) and the c axis (κ_c), for two samples with sizes of $3.5 \times 1.68 \times 0.59$ mm³ and $3.1 \times 1.50 \times 0.51$ mm³, respectively. Details for the measurements have been described elsewhere.^{27–29}

Figure 1(c) shows the temperature dependencies of κ_b

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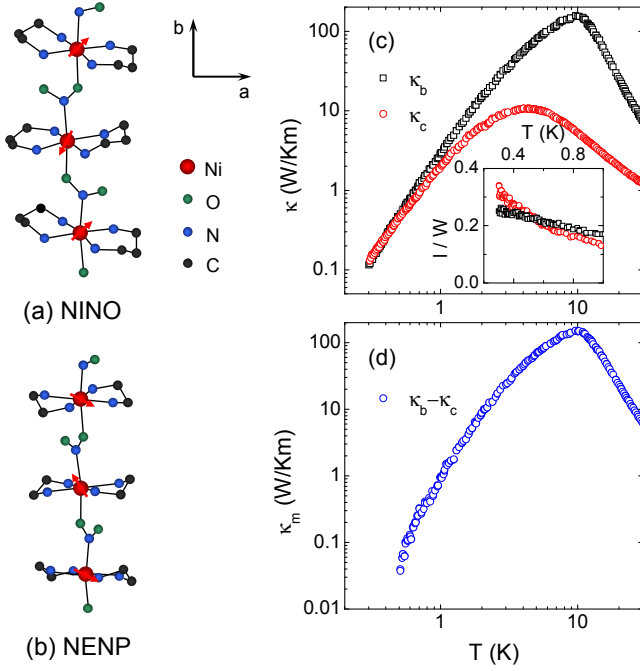


FIG. 1. (color online) (a,b) Schematic view of the spin-chain structure of NINO and NENP (Ref. 21). In zero field, the Ni^{2+} spins show a (disordered) ground state of the Haldane gap state. (c) Temperature dependencies of the thermal conductivities κ_b and κ_c of NINO single crystals in zero magnetic field. The inset shows the temperature dependencies of the ratio of the phonon mean free path l to the averaged sample width W . (d) Magnetic thermal conductivity $\kappa_m(T)$ obtained from $\kappa_b - \kappa_c$.

and κ_c of NINO single crystals in zero magnetic field. Apparently, the behaviors of κ_b and κ_c seem to be different from usual phonon transport properties of insulators.³⁰ In nonmagnetic insulators, the position and the magnitude of the low- T phonon peak are mainly determined by the impurity/defect scattering on phonons. Therefore, the phonon peaks are usually located at similar temperatures for different directions of heat currents and the shapes (temperature dependencies) of peaks are almost identical for different directions. These are clearly different to what the NINO data show. The most remarkable phenomenon in Fig. 1(c) is that the κ_b and κ_c differ significantly at relatively high temperatures, but they are almost the same at subKelvin temperatures. All these features suggest that the heat transport of NINO cannot be a simple phononic behavior. One may naively expect that the difference is due to the additional magnetic thermal transport along the chain direction. However, the separation of phononic and magnetic conductivities from the experimental data is not so straightforward. A common way to obtain the magnetic thermal conductivity in the quasi-1D magnets is to assume that the phonon term along the spin-chain direction can be estimated from the thermal conductivity perpendicular to the spin chain.^{2,3} The main uncertainty of this method is related to the

anisotropy of the phonon thermal transport itself, which is known to be insignificant for most materials (with some exceptions like those having layered lattices).³⁰

In an earlier work, another Haldane chain compound, NENP, was found to exhibit an anisotropic phonon thermal conductivity even at subKelvin temperatures.²⁰ The magnetic thermal conductivities of NENP were obtained from the magnetic-field-induced increase of κ along the spin chain.²⁰ In our data, however, the κ_b and κ_c are nearly the same at very low temperatures. This indicates an isotropic phonon transport at such low temperatures, where the magnetic excitations are negligible. In this regard, it is useful to estimate the mean free path of phonons, l , by using the kinetic formula $\kappa_{ph} = \frac{1}{3}Cv_pl$, where $C = \beta T^3$ is the phonon specific heat at low temperatures and v_p is the averaged sound velocity.^{28,31} The phonon specific-heat coefficient β is known from the specific heat measurements,²⁶ and v_p can be obtained from β . The inset to Fig. 1(c) shows the temperature dependencies of the ratio l/W for κ_b and κ_c , where W is the averaged sample width. It is found that in both cases the l becomes comparable to W at $T \rightarrow 0.3$ K, indicating that the phonon heat transport approaches the boundary scattering limit.^{28,30,31} With increasing temperature, the κ_b and κ_c show a large difference because the magnetic excitations become populated and they can either transport heat along the spin-chain direction or scatter phonons in other directions.

We can estimate the magnetic thermal conductivity along the spin chain by subtracting the κ_c from κ_b . As shown in Fig. 1(d), the magnetic thermal conductivity is very large and reaches a value of ~ 150 W/Km at 10 K. Thus, this compound has larger thermal conductivity than many other low-dimensional quantum magnets.^{1-3,13,14,20}

The magnetic-field dependencies of κ_b and κ_c have been measured at low temperatures and in fields along the a axis. As shown in Fig. 2, both the κ_b and κ_c show weak field dependencies except in the vicinity of 9 T, which is known to be the critical field of this material. Apparently, at the critical field, the spin gap is minimized and therefore the magnetic excitations are well populated. The dip-like $\kappa_c(H)$ clearly shows the strong suppression of phonon transport due to scattering by magnetic excitations. This result indicates that magnetic excitations also play a role in the heat transport as phonon scatterers in this direction. In the spin-chain direction, the increase of magnetic excitations leads to a peak of $\kappa_b(H)$ at the critical field. This again demonstrates that the magnetic excitations in this material can transport heat directly in the spin-chain direction. Therefore, the $\kappa(H)$ behaviors shown in Fig. 2 are supportive for the above understanding of the zero-field heat transport data. At very low temperatures, the ~ 8 K gap impedes the low-energy magnetic excitations and the phonon transport is dominated, which results in a nearly isotropic thermal transport. With increasing temperature, the magnetic excitations become more

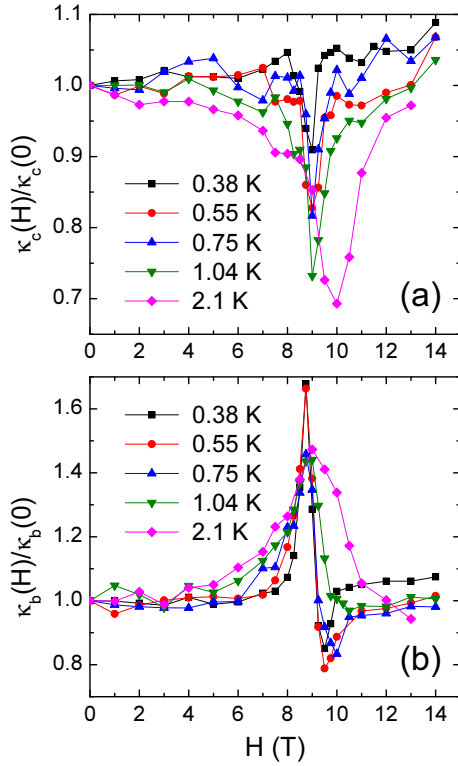


FIG. 2. (color online) Magnetic-field dependencies of κ_c and κ_b of NINO single crystals in magnetic field parallel to the a axis.

populated and they take part in the heat transport by acting as heat carriers in the spin-chain direction and as phonon scatterers in other directions. Thus, the κ_b and κ_c show a large difference at relatively high temperatures. The present experimental phenomena are very similar to those in NENP. However, the effect of magnetic excitations scattering phonons was not observed in NENP.²⁰ Another difference is that the relative increase of κ at H_c is 4–6 times larger in NENP. However, since the absolute magnitude of κ is more than 10 times smaller in NENP, the field-induced increase of magnetic thermal conductivity is actually stronger in NINO.

In summary, we observe a strongly anisotropic heat transport along the spin-chain direction and the vertical direction in NINO single crystals. This indicates that the $S = 1$ chain system can also have larger magnetic thermal conductivity. It is essentially consistent with the recent results on another Haldane chain compound, NENP, in which magnetic thermal transport was evidenced when the spin gap was suppressed by magnetic field.²⁰ It is necessary to investigate the origin of the remarkably different ability of spin transport in many $S = 1$ chain compounds.

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